Evaluation of Tris-CMPO and Tris-CMPS Ligands as Extractants for Actinide/Lanthanide Separation

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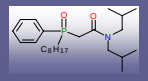
Separation of Lanthanides and Actinides

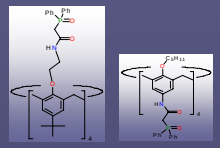
Efficient protocols for the separation of actinide and lanthanide ions are required for the processing of acidic nuclear waste streams. Because actinide and lanthanide ions are similar in size and charge, the development of methods to selectively bind actinide(III) ions in the presence of lanthanide(III) metals have proven to be especially problematic. Several different techniques to facilitate this separation such as selective precipitation, ion chromatography, and liquid-liquid extraction techniques are currently in use with varying degrees of success.

One of the more successful separation strategies uses simple molecules with the CMPO (carbamoylmethyl-phosphine oxide) moiety to separate trans-uranium metals from lower atomic number elements. The selectivity of this trans-uranium extraction (TRUEX) process must be improved for more demanding systems.



octyl(phenyl)-N,N-diisobutyl-CMPO (used in the TRUEX process)

NMR analysis of the extracted species in the TRUEX process suggest a 3:1 CMPO:actinide(III) stoichiometry (including the 3 nitrate counterions). A similar coordination environment was realized by Böhmer *et al.* in which four CMPO moieties were tethered to calix[4]arenes. Overall, improvements in actinide selectivity against some of the lanthanides (see extraction results below).



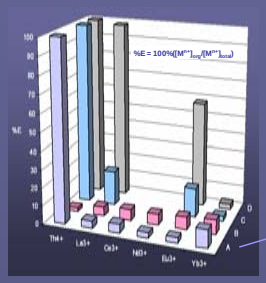
Lower and upper rim calix[4]arene CMPO ligand systems

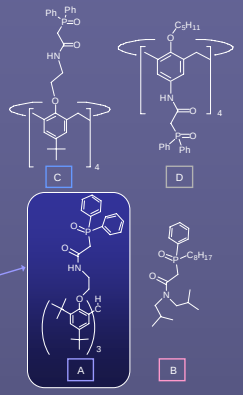
Inspired by the calixarene system, we have synthesized a tris-CMPO ligand that accurately mimics the proposed TRUEX process stoichiometry and selectively extracts actinide thorium(IV) ions over all of the lanthanides. We have also isolated and characterized various metal/ligand complexes that allows us to better understand the mechanism of this selectivity.

The successful separation method for actinides over trivalent lanthanides must exploit the slight differences in ionic radii and covalency/polarizability of these metal ions. Materials with the greatest potential for increased covalent interactions provide the most significant opportunity for successful Ln(III)/An(III) separation; therefore, soft donor ligands containing S or N groups are often employed. In this light, a new tris carbamoylmethylphosphine sulfide (tris-CMPS) ligand system was designed containing three phosphine sulfide donors rather than phosphine oxide found in the tris-CMPO system. The three soft sulfur atoms were expected to increase interactions with Am(III) upon complex formation, significantly enhancing the ability of our ligand system to discriminate between An(III) and Ln(III) ions in acidic solutions.

A Comparative CMPO Th/Ln Extraction

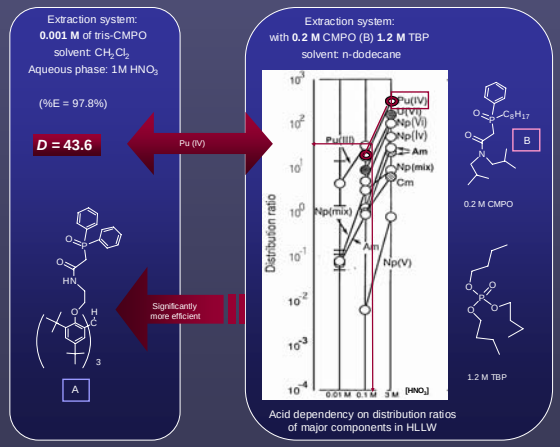
Extraction experiments in equal volumes 10^{-4} M metal in 1M HNO_3 and 10^{-3} M ligand in CH_2Cl_2





The tris-CMPO ligand exhibits much higher selectivity for the actinide thorium over the entire lanthanide series in comparison to other multi-CMPO and classical CMPO extractants.

Comparison of CMPO Ligands for Pu(IV) Binding



Acid dependency on distribution ratios of major components in HLLW

Concentration of A vs. CMPO (B) 1/200!
No TBP required
Non-optimized conditions

Conclusions and Future Work

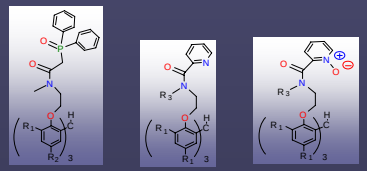
The tris-CMPO molecule has been found to be an effective extractant for tetravalent Th and Pu. In general, the tris-CMPO ligand system shows promise as an improved extractant for tetravalent actinide recoveries from high level liquids waste. A simple one-stage extraction process can separate over 97% of Pu from fission products. The ligand system was found to be a more selective extractant then its calix[4]arene counterparts as well as the CMPO molecule itself. In fact, a 200-fold concentration of the synergistic mixture of CMPO and TBP is necessary to obtain the same Pu(IV) distribution coefficient with respect to tris-CMPO.

The selectivity of the standard tetravalent actinides extractant, (*N,N*-diisobutylcarbamoylmethyl) octylphenylphosphineoxide (CMPO), was strongly improved by the attachment of three CMPO-like functions on the triphenoxymethane platform. The data clearly demonstrate intramolecular cooperative binding of these three ligating groups confirmed by compositional and structural analysis of the extracted complexes. In addition, it was found that the presence of three preorganized CMPO moieties is crucial to fulfill the geometry requirements around metal center to afford appreciable extraction percentage. However, the combination of the three ligating functions of the CMPO-type is not the only factor in determining its complexation effectiveness. Evidently, the ligands mutual orientation and their flexibility also have an important influence. It can be assumed that an appropriate balance between rigidity and flexibility of the basic skeleton may also be crucial for efficient coordination.

The substitution of phosphine oxide with softer phosphine sulfide induced a loss of selectivity for tetravalent actinides. Moreover, the tris-CMPS extractant did not show the expected ability to discriminate between An(III) over Ln(III).

Due to the almost unlimited structural and chemical modifications of tris-CMPO/CMPO ligand systems, it can be expected that more effective extractants for trivalent An/Ln separation can be obtained.

Ligand Modifications in Progress



R_1 = methyl, *i*-propyl, *t*-butyl, *t*-pentyl
R_2 = *t*-butyl, *t*-pentyl
R_3 = methyl, H

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